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# Polymerization of Fluoroalkyl Polyhedral Oligomeric Silsesquioxane (F-POSS) Macromers

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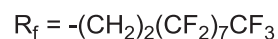
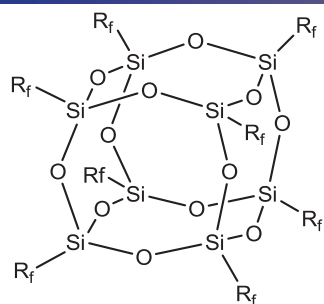
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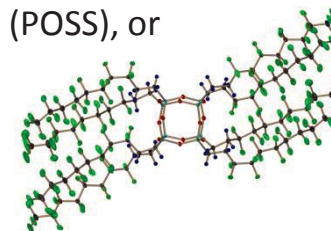


# Introduction to F-POSS



(1,1,2,2-tetrahydroperfluorodecyl)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> Polyhedral Oligomeric Silsesquioxane (POSS), or fluorodecyl POSS

- hybrid organic-inorganic structure
- well-defined polyhedral architecture
- long-chain fluoroalkyl substituents on periphery of cage



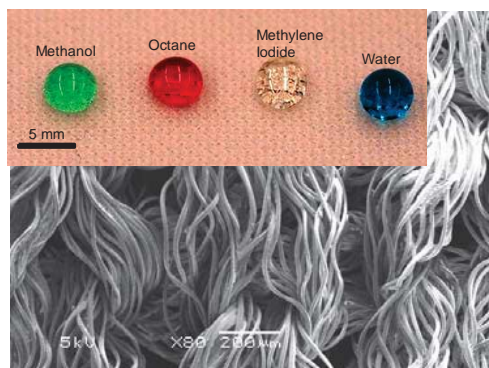
Due to its unique structure, fluorodecyl POSS has one of the lowest surface energies of any crystalline solid currently known

- |                             |            |
|-----------------------------|------------|
| - fluorodecyl POSS          | 9.3 mN/m   |
| - polytetrafluoroethylene   | 18-20 mN/m |
| - CF <sub>3</sub> monolayer | 6.7 mN/m   |

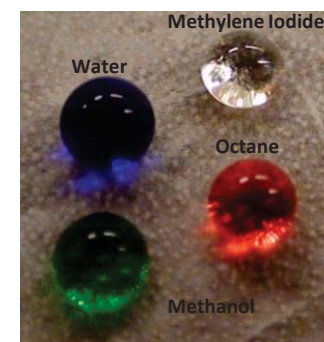
Low surface energy and other unique properties of fluorodecyl POSS has enabled the development of various types of tunable non-wetting polymeric surfaces



Superhydrophobic/oleophilic dip-coated fabric  
Tuteja *et al*, Science, **2007**, 318, 1618



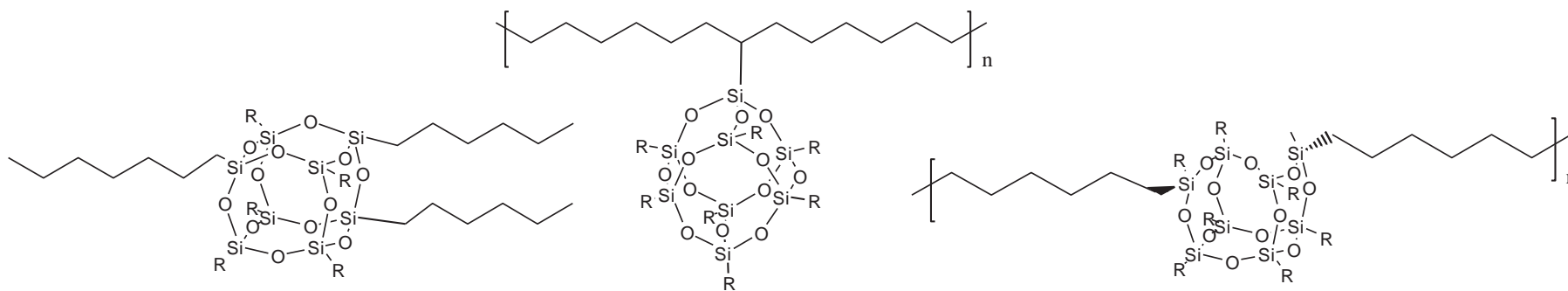
Superamphiphobic dip-coated fabric  
Choi *et al*, Adv Mater, **2009**, 21, 2190



Superamphiphobic electrospun surfaces  
Tuteja *et al*, PNAS, **2008**, 105, 18200



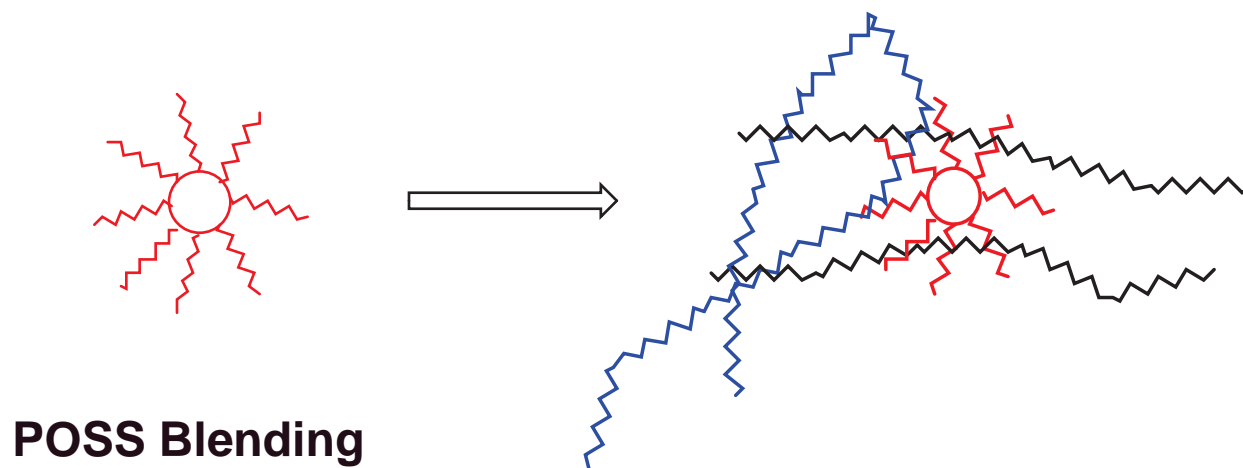
# POSS Incorporation in Polymers



**Cross-linker**

**Pendant Polymer**

**Bead Copolymer**



**POSS Blending**

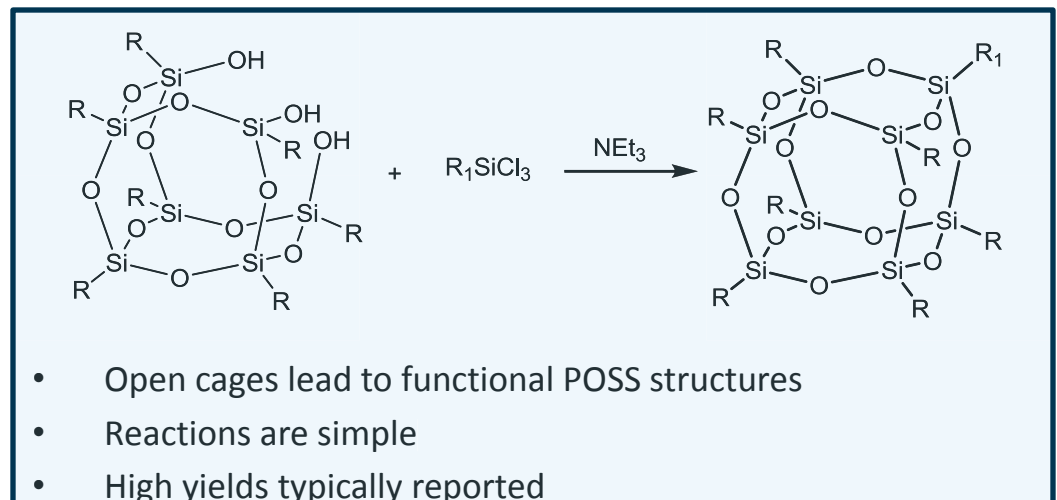
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Cordes, D. B.; Lickiss, P. D.; Rataboul, F., *Chem. Rev.* 2010, 110 (4), 2081-2173. Phillips, S. H.; Haddad, T. S.; Tomczak, S. J., *Curr. Opin. Solid State Mater. Sci.* 2004, 8, 21-29 Iacono, S. T.; Buddy, S. M.; Mabry, J. M.; Jr., D. W. S., *Polymer* 2007, 48, 4637-4645. Koh, K; et. al., *Macromolecules* 2005, 38, 1264-1270.



# Functional F-POSS (Open-Caged)

- Close-caged structures are accessible and have proven versatile in polymer composites
  - Limitations
    - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
  - Open door for use a *building block* material for *low surface energy materials*
- Applications
  - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
    - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
  - Effects on polymer composite properties
    - Wetting, phase behavior, solubility, etc....





# Methods to Produce Incompletely Condensed Silsesquioxanes



- Bottom-up approach
  - Acid or base mediated from  $\text{RSiCl}_3$  or  $\text{RSi(OR)}_3$
  - Condensation reaction
  - Balance of stoichiometry, temperature, reaction time, patience, and luck
  - Stopping POSS synthesis early, before cages closes
  - More common approach
- Top-down Approach
  - Strong acid or base mediated
  - Starting from a POSS cage
  - Conversion of Si-O-Si bonds to Si-O<sup>(-)</sup> C<sup>(+)</sup> or Si-OH bonds
  - Opening up POSS cage

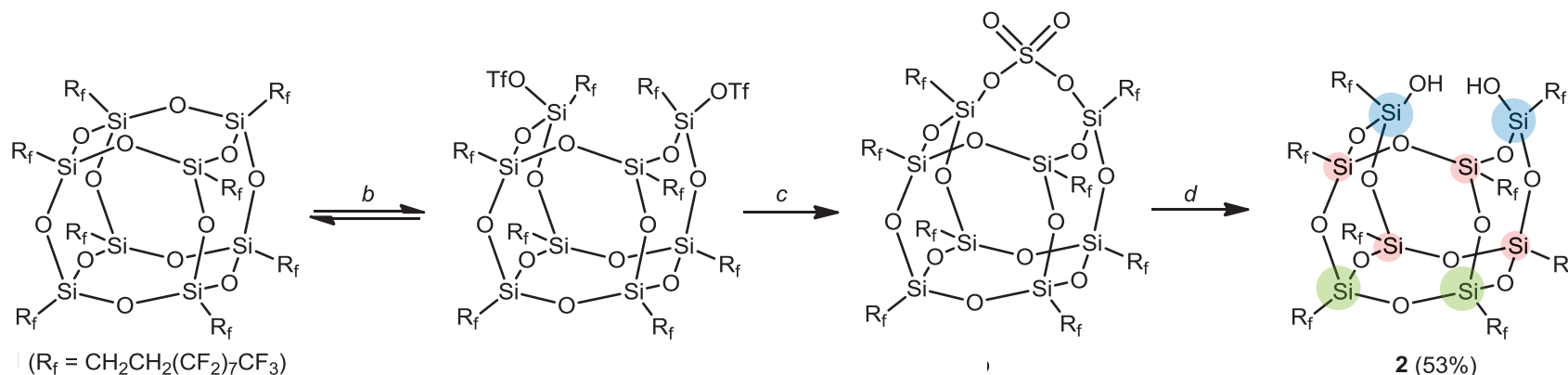
Which method can be applied to long-chain F-POSS?

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Feher, F. J.; Terroba, R.; Ziller, J. W. *Chemical Communications* **1999**, 2309. Feher, F. J.; Newman D.A.; Walzer, J.M., *J. Am. Chem. Soc.*, **1989**, 111, 1741. Feher, F. J.; Soulivong, D.; Nguyen, F.; Ziller, J. W. *Angew.Chem. Inter. Ed.* **1998**, 37, 2663. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* **1998**, 1279.

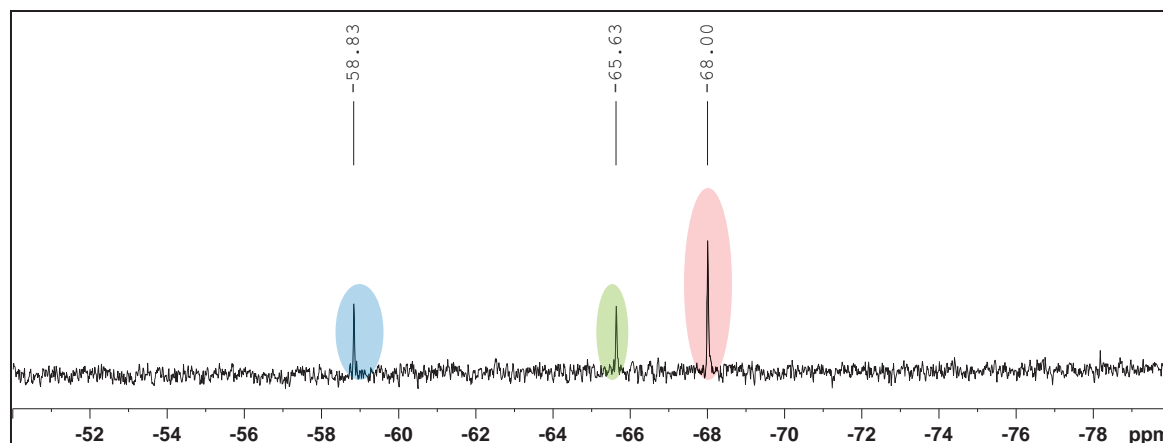


# Incompletely Condensed Silsesquioxane



<sup>a</sup>Conditions: All reactions were performed in  $\text{C}_6\text{F}_6$  at 25 °C. <sup>b</sup> $\text{CF}_3\text{SO}_3\text{H}$ , 75 mins. <sup>c</sup> $\text{NBut}_4\text{HSO}_4$ , 30 mins, <sup>d</sup> $(\text{CF}_3)_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (10:1), 12 hrs.

<sup>29</sup>Si NMR in  $\text{C}_6\text{F}_6$  of disilanol F-POSS



- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.

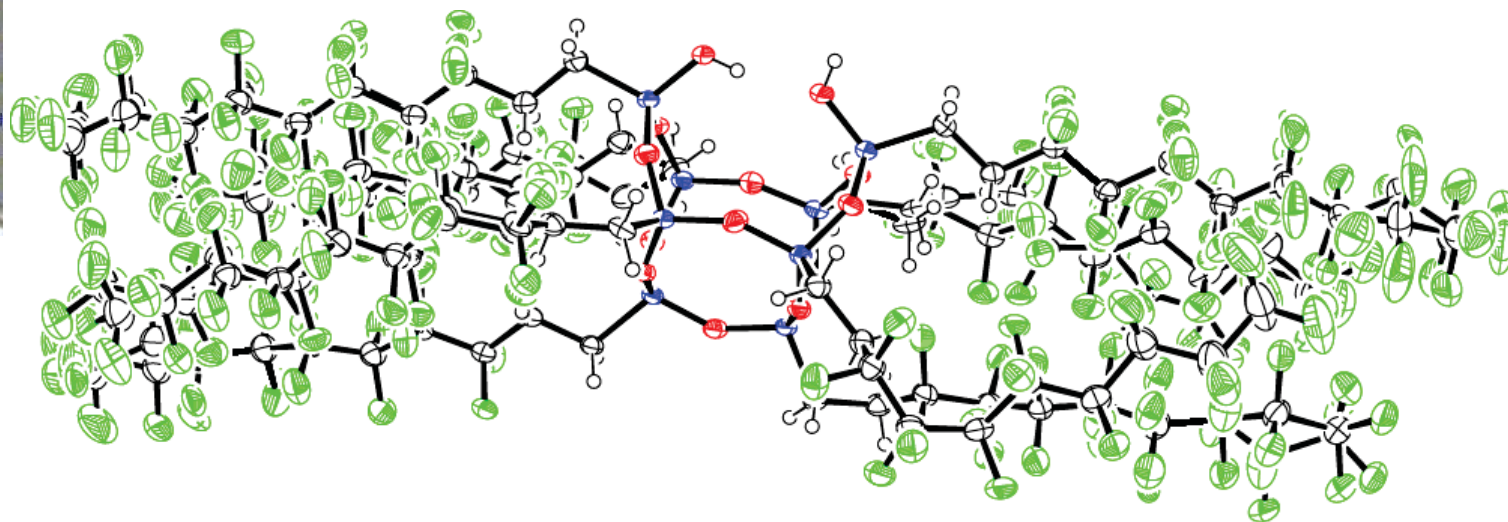
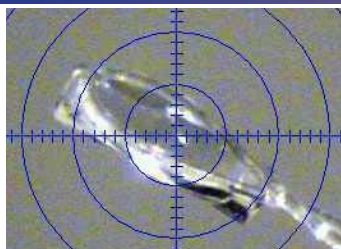
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Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, 2011, 133, 20084.

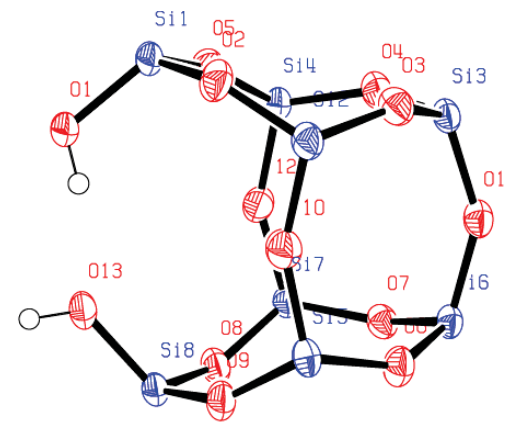
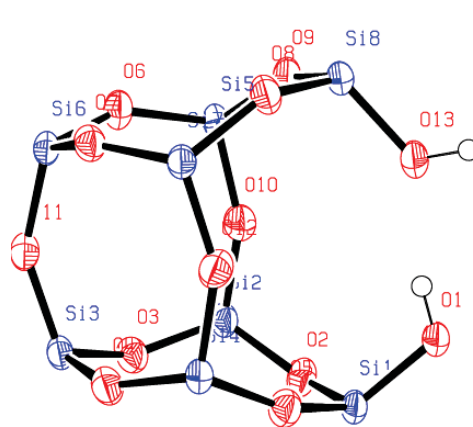




# X-Ray Crystal Structure of Disilanol



- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- $M_r$  = monoclinic, space group  $P2(1)/c$ ,  $a=11.84(10)$  Å,  $b=57.11(6)$  Å,  $c=19.06(2)$  Å,  $\alpha=90.00^\circ$ ,  $\beta=92.21(10)^\circ$ ,  $\gamma=90.00^\circ$ ,  $V=12878(2)$  Å<sup>3</sup>

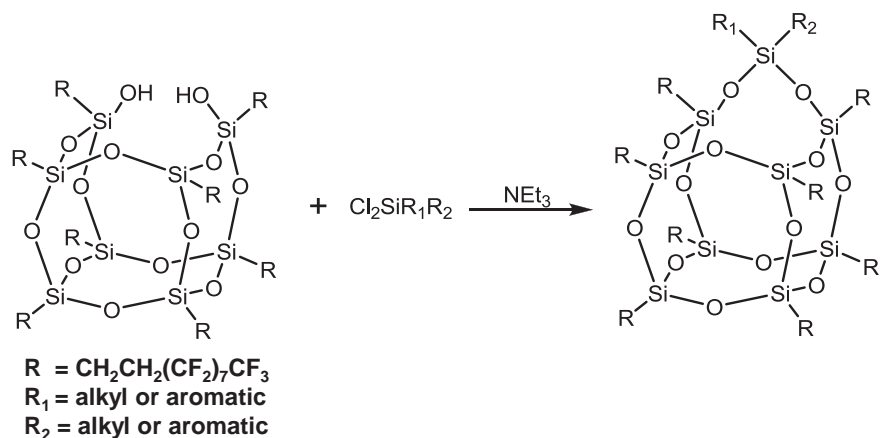


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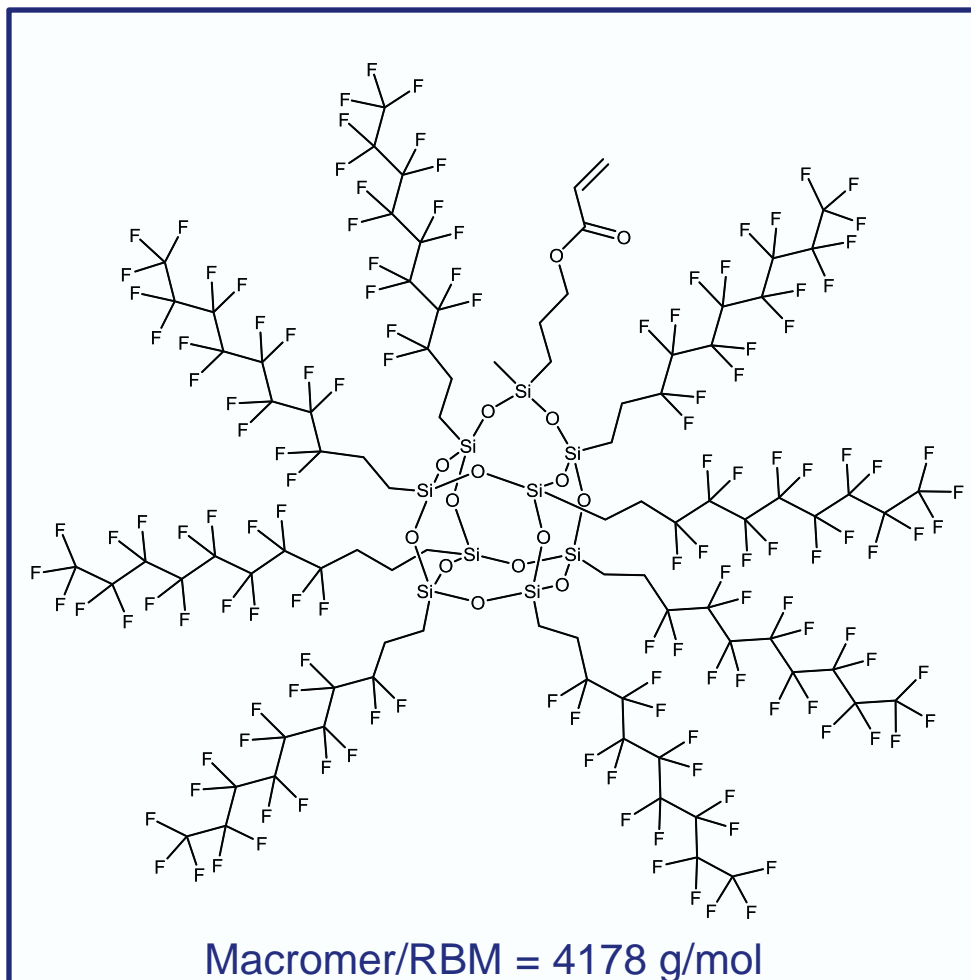




# Edge Capping Reactions



- Edge capping reactions typically have 40-90% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction

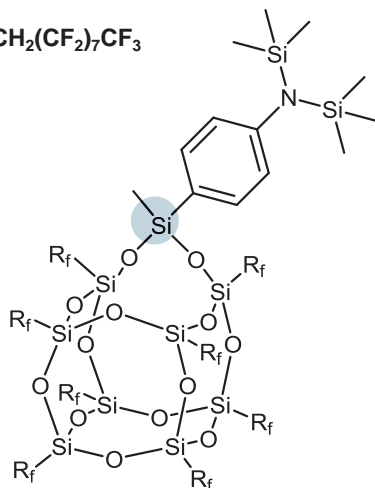


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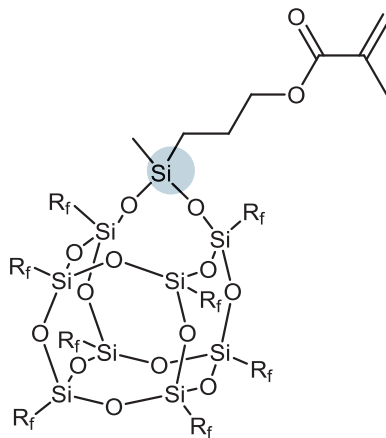


# $^{29}\text{Si}$ NMR of F-POSS Structures

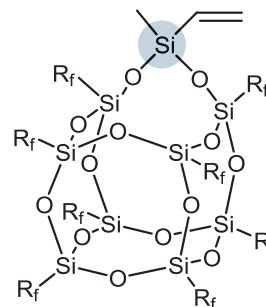
$\text{R} = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$



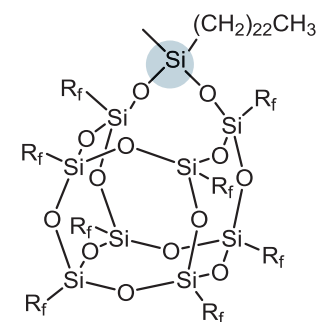
-29.5 ppm



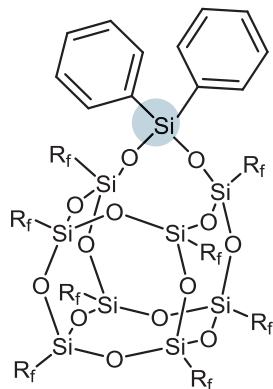
-17.8 ppm



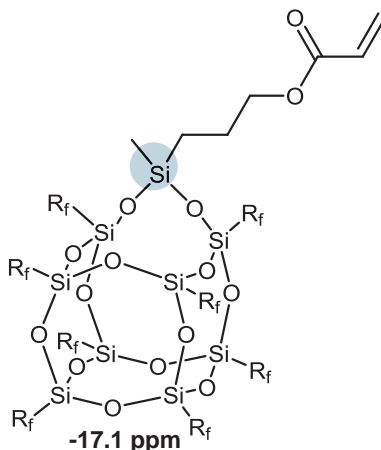
-32.1 ppm



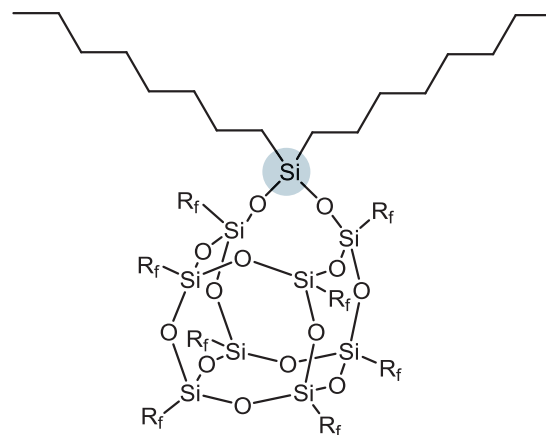
-17.8 ppm



-45.5 ppm



-17.1 ppm



-17.9 ppm

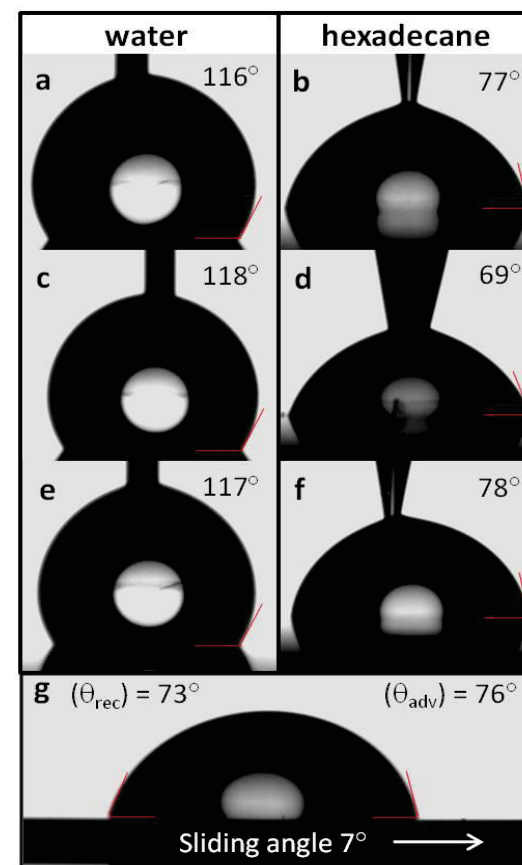
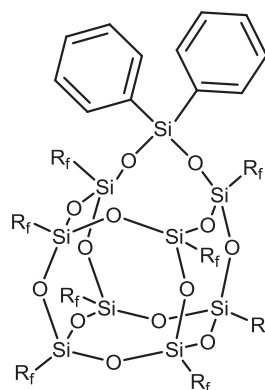
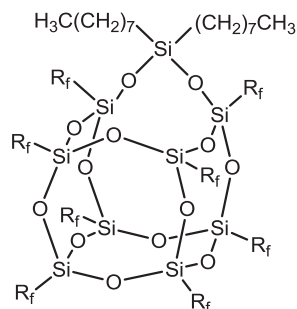
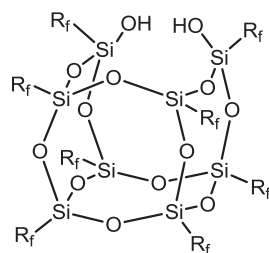
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Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Stone, R.T.; Haddad, T.S.; Mabry, J.M., J. Am. Chem. Soc., 2011, 133, 20084.



# Contact Angle Measurements

- Non-wetting surfaces can be developed by a combination of three parameters
  - Chemical functionality (high fluorine content)
  - Roughness (micro- and nanoscale)
  - Surface Geometry (re-entrant curvature)
- What type of influence will functional groups have on F-POSS surface properties?*
- Solvent impact?*

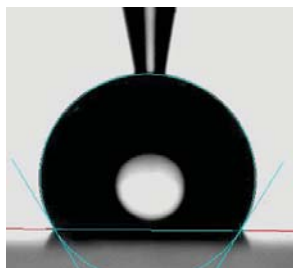


Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10  $\mu$ L) rolling off surface coated with compound **diphenyl** (g).

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# Dynamic Contact Angle Measurements



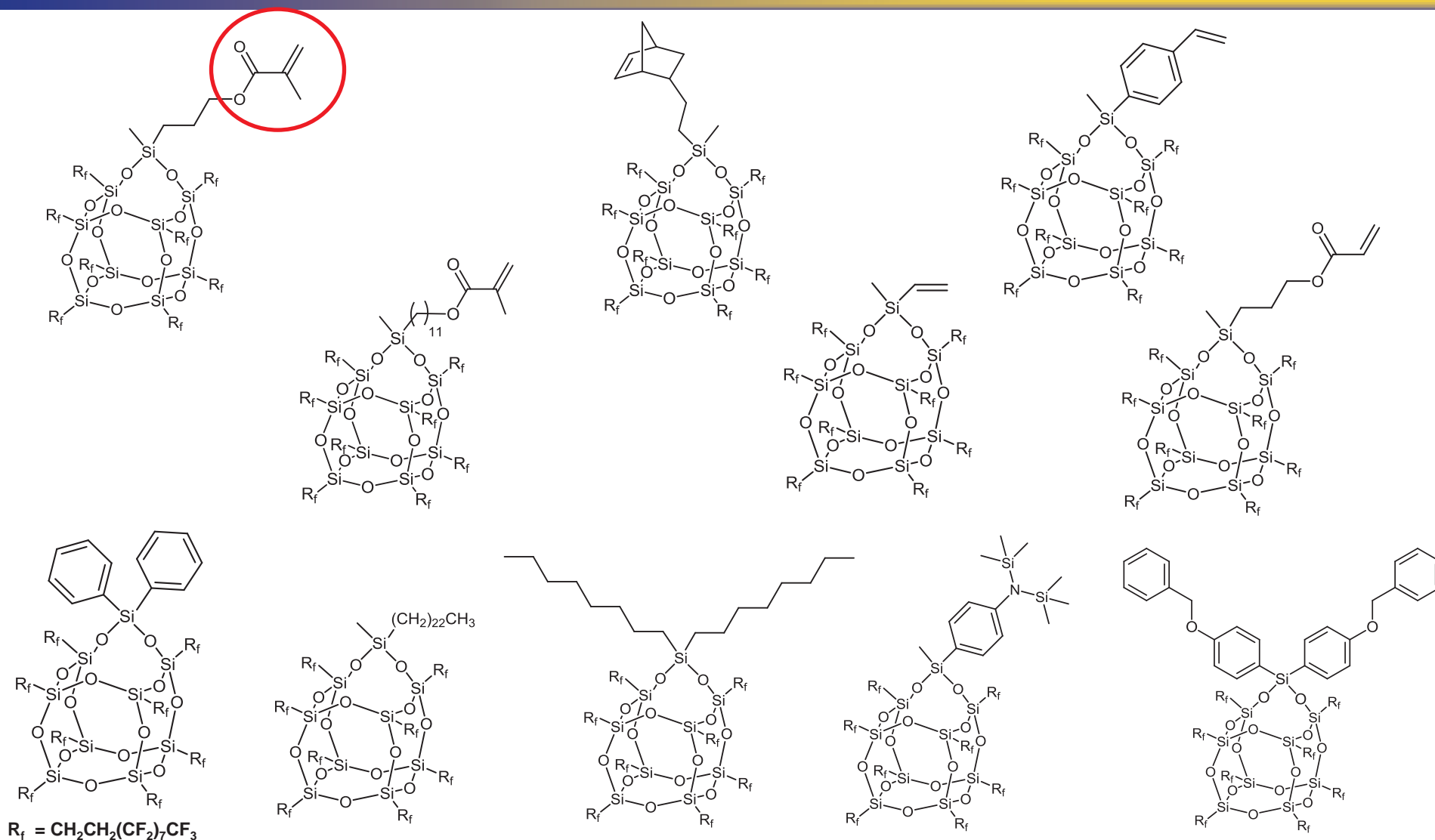
<i>Functional Group on F-POSS</i>	<i>water</i>		<i>hexadecane</i>	
	( $\theta_{adv}$ )	( $\theta_{rec}$ )	( $\theta_{adv}$ )	( $\theta_{rec}$ )
F-POSS*	$124 \pm 0.5^\circ$	$109.6 \pm 0.7^\circ$	$79.1 \pm 0.4^\circ$	$65.1 \pm 0.5^\circ$
Si-(OH) <sub>2</sub>	$116.8 \pm 0.4^\circ$	$111 \pm 0.6^\circ$	$77.4 \pm 0.4^\circ$	$74.4 \pm 0.8^\circ$
Si-(CH <sub>3</sub> )(CH=CH <sub>2</sub> )	$116.2 \pm 0.4^\circ$	$100.6 \pm 0.8^\circ$	$78.4 \pm 0.3^\circ$	$70.6 \pm 2.3^\circ$
Si((CH <sub>3</sub> )((CH <sub>2</sub> ) <sub>3</sub> OC(O)CCH=CH <sub>2</sub> ))	$118.2 \pm 1.0^\circ$	$90.6 \pm 1.0^\circ$	$76.8 \pm 0.3^\circ$	$64.8 \pm 1.0^\circ$
Si-(CH <sub>3</sub> )( (CH <sub>2</sub> ) <sub>3</sub> OC(O)C(CH <sub>3</sub> )=CH <sub>2</sub> )	$117.1 \pm 0.6^\circ$	$93.8 \pm 1.5^\circ$	$78.1 \pm 0.4^\circ$	$63.0 \pm 1.2^\circ$
Si-(CH <sub>3</sub> )((CH <sub>2</sub> ) <sub>22</sub> CH <sub>3</sub> )	$117.9 \pm 0.4^\circ$	$96.9 \pm 1.9^\circ$	$78.0 \pm 0.4^\circ$	$16.2 \pm 5.5^\circ$
Si-(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	$116.2 \pm 0.4^\circ$	$110.5 \pm 0.5^\circ$	$76.0 \pm 0.8^\circ$	$73.2 \pm 0.4^\circ$
Si-((CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> ) <sub>2</sub>	$117.9 \pm 0.5^\circ$	$95.5 \pm 0.4^\circ$	$69.1 \pm 1.2^\circ$	$23.1 \pm 1.2^\circ$

Samples (10 mg/mL) were spin casted on oxygen-plasma cleaned Si wafers at 900 rpm for 30 seconds. Contact angle measurements were run in triplicate. Surface roughness < 5nm (AFM and Optical Profilometry).

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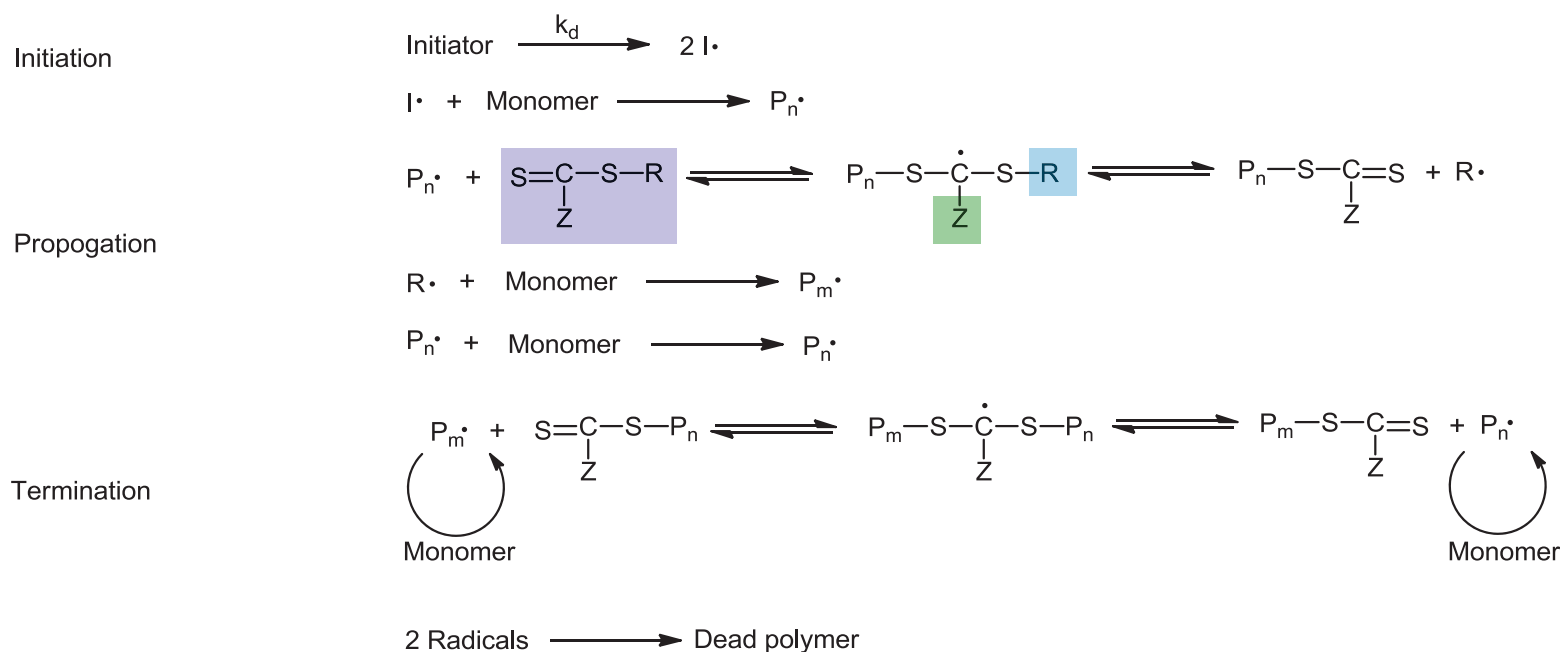
# F-POSS Structures Synthesized



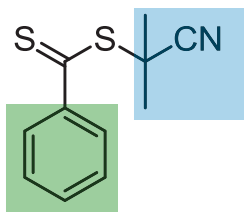
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# Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization



## Chain Transfer Agent



## RAFT Polymerization

- Controlled polymerization
- Allows for block copolymers
- Tune molecular weight

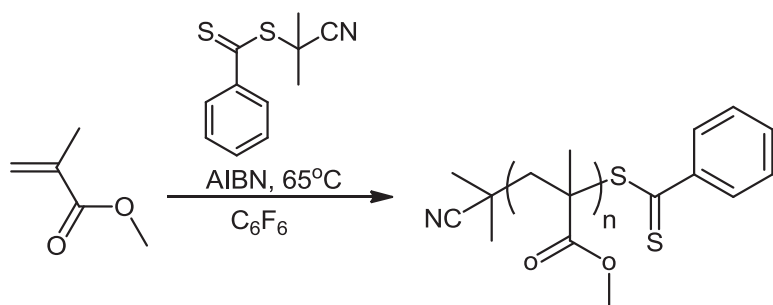
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Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H., *Macromolecules* 1998, 31, 5559–5562.  
Moad, G.; Biccocchi, E.; Chen, M.; Chiefari, J.; Guerrero-Sanchez, C.; Haeussler, M.; Houshyar, S.; Keddie, D.; Rizzardo, E.; Thang, S. H.; Tsanakisidis, J., *ACS Symp. Ser.* 2012, 1100, 243-258.

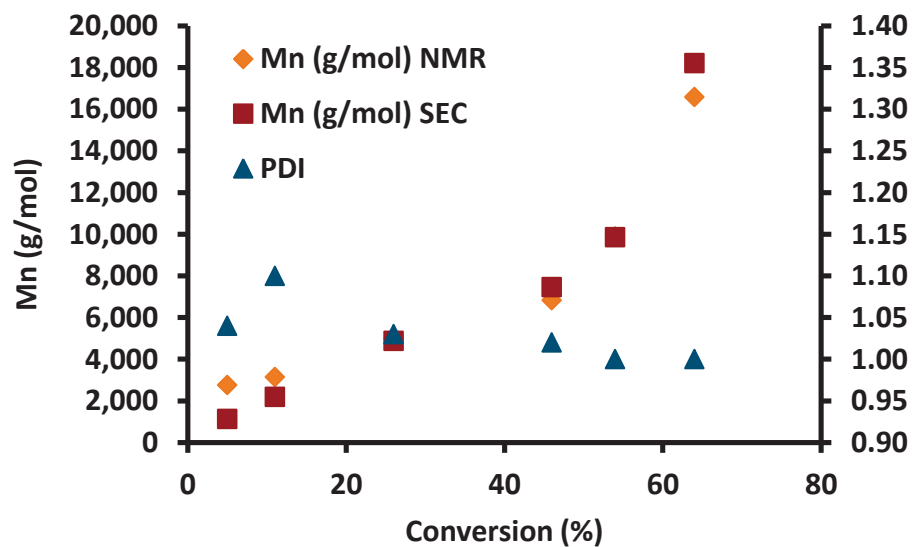
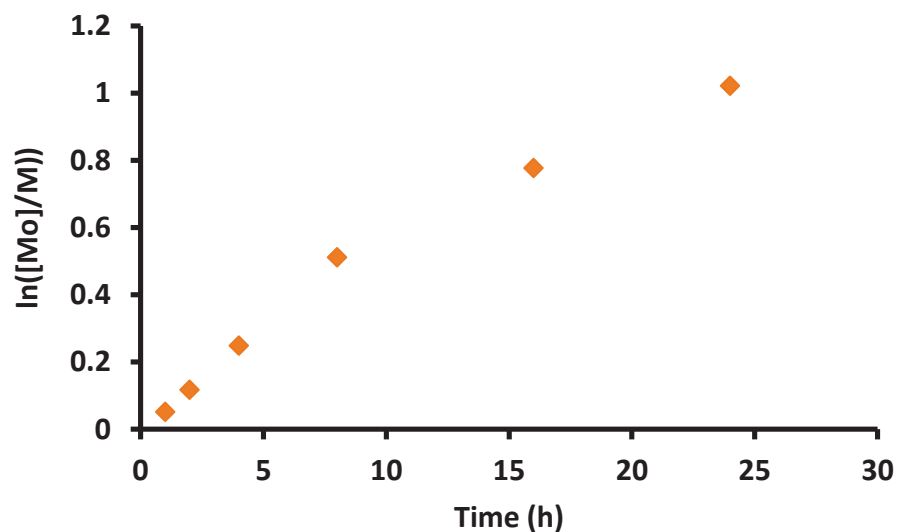




# RAFT polymerization of MMA in $C_6F_6$



- Testing RAFT in fluorinated solvent
- RAFT polymerization proceeds in  $C_6F_6$
- Best control in first 10 hours

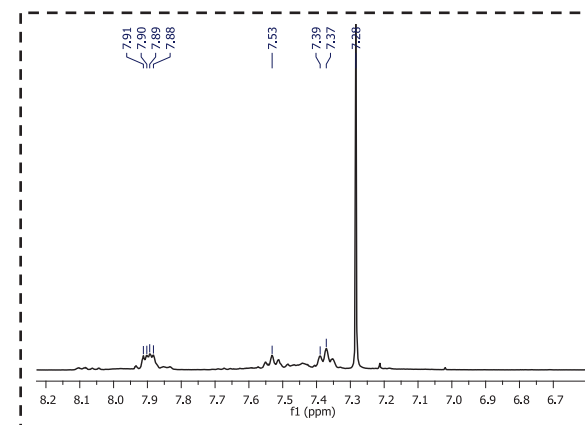
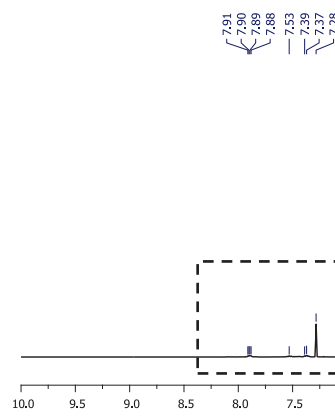
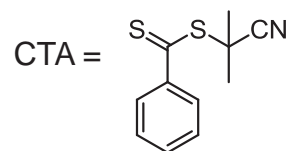
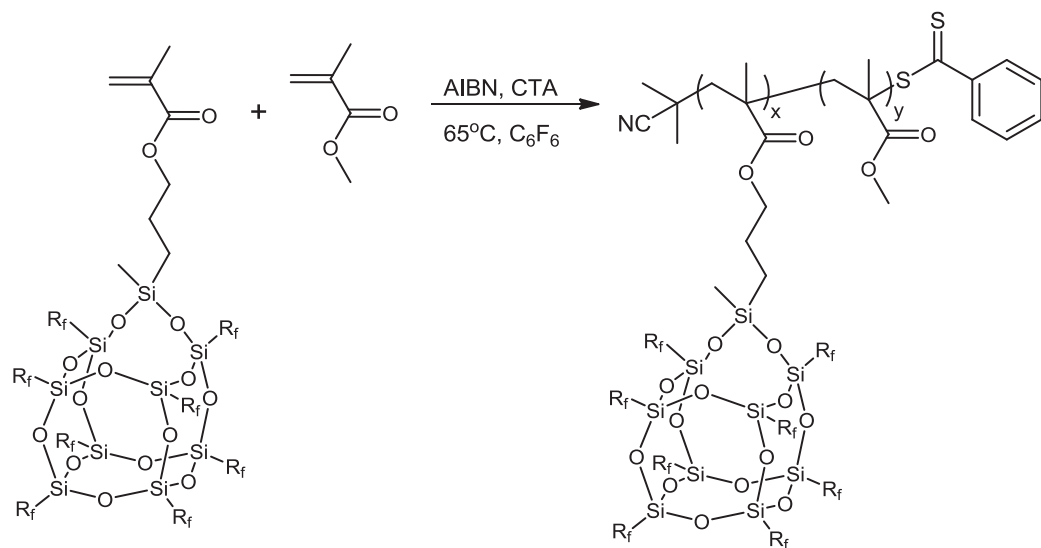


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SEC MALLS: RI and LS detector (Wyatt), 1.0 mL/min, 30 min, THF.



# RAFT copolymerization of P(F-POSS-MA)-co-PMMA



$R_f = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$

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<sup>1</sup>H NMR in CDCl<sub>3</sub>



# RAFT copolymerization of P(F-POSS-MA)-co-PMMA



F-POSS		$M_w$		Conv.	water		hexadecane	
wt %	(g/mol)	PDI	%	$(\theta_{adv})$	$(\theta_{rec})$	$(\theta_{adv})$	$(\theta_{rec})$	
F-POSS-MMA				$117.1 \pm 0.6^\circ$	$93.8 \pm 1.5^\circ$	$78.1 \pm 0.4^\circ$	$63.0 \pm 1.2^\circ$	
0	58,100	1.05	73	$77.8 \pm 1.3^\circ$	$57.8 \pm 2.5^\circ$	wetted	wetted	
1	58,700	1.08	72	$109.2 \pm 2.4^\circ$	$61.5 \pm 1.9^\circ$	$67.8^\circ \pm 1.4$	wetted	
5	23,000	1.01	30	$117.8 \pm 1.6^\circ$	$95.7 \pm 5.9^\circ$	$76.7 \pm 1.1^\circ$	$68.8 \pm 1.9^\circ$	
10	26,600	1.01	29	$118.2 \pm 1.4^\circ$	$101.1 \pm 2.5^\circ$	$77.2 \pm 0.4^\circ$	$69.5 \pm 2.1^\circ$	
25	37,700	1.03	41	$120.8 \pm 97.0^\circ$	$97.0 \pm 2.4^\circ$	$82.9 \pm 0.4^\circ$	$74.6 \pm 2.0^\circ$	

SEC-MALLS conditions: 25°C, flow rate (1 mL/min), solvent (Asahiklin-225 [mixture of dichloropentafluoropropanes]), concentration measured with RI detector. Contact angle conditions: polymer solutions (20 mg/mL) were spun cast on SiO<sub>2</sub> wafers at 900 rpm.

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Isemura, T.; Kakita, R.; Kawahara, K., *Journal of Chromatography A* 2004, 1026, 109-1196.

Wesdemiotis, C.; Pingitore, F.; Polce, M. J.; Russell, V. M.; Kim, Y.; Kausch, C. M.; Connors, T. H.; Medsker, R. E.; Thomas, R. R., *Macromolecules* 2006, 39, 8369-8378.

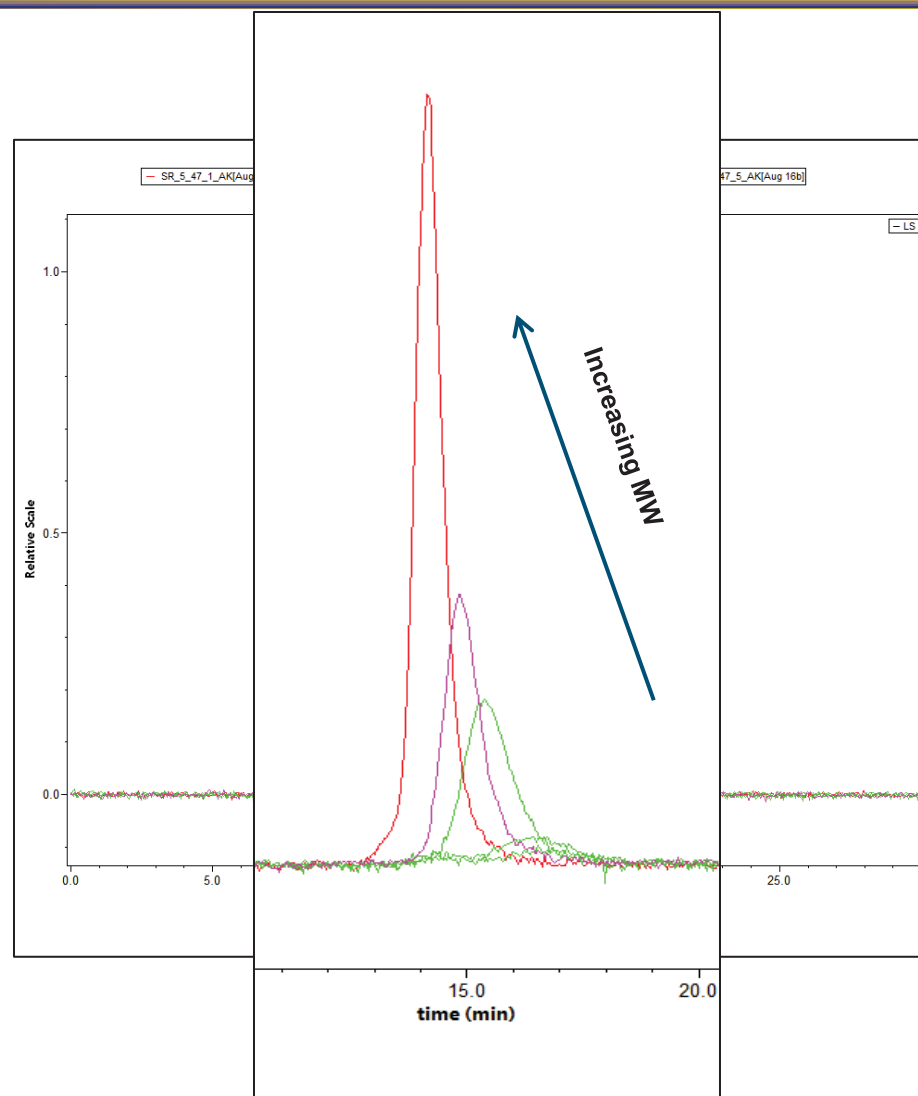


# RAFT copolymerization of P(F-POSS-MA)-co-PMMA



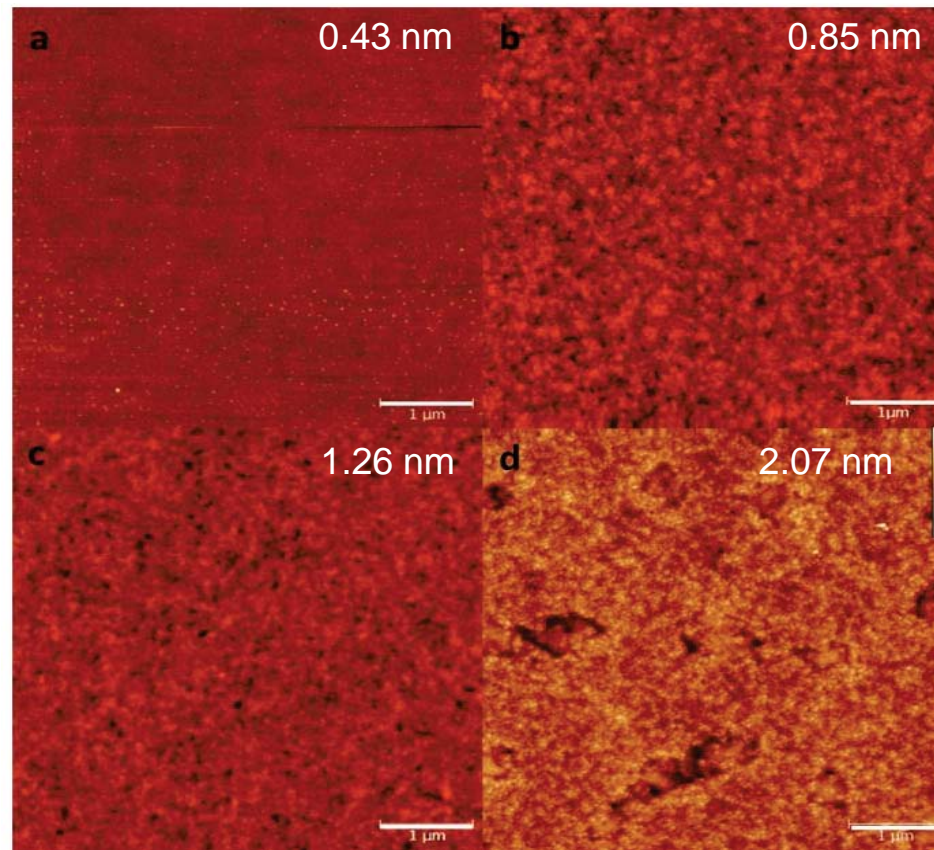
10% F-POSS	$M_n$		Conv.
Time (hr)	(g/mol)	PDI	%.
1	4100	2.2	8
2	4,700	1.2	16
4	11,300	1.04	28
8	26,600	1.03	51

- **Determining impact of F-POSS on polymerization conditions**
  - No homopolymerization possible
  - Polymerization difficult above 50 wt % F-POSS-MMA loading





# AFM of P(F-POSS-MA)-co-PMMA



AFM image of spun cast films of a) 1 wt. % b) 5 wt. %. c) 10 wt. % and d) 25 wt.% F-POSS copolymer on  $\text{SiO}_2$  from a 10 mg/mL concentrated solution in Asahiklin-225 at 900 rpm. Each image is shown with a z-scale of 0–10 nm. Top corner of each image root mean squared (rms) surface roughness.

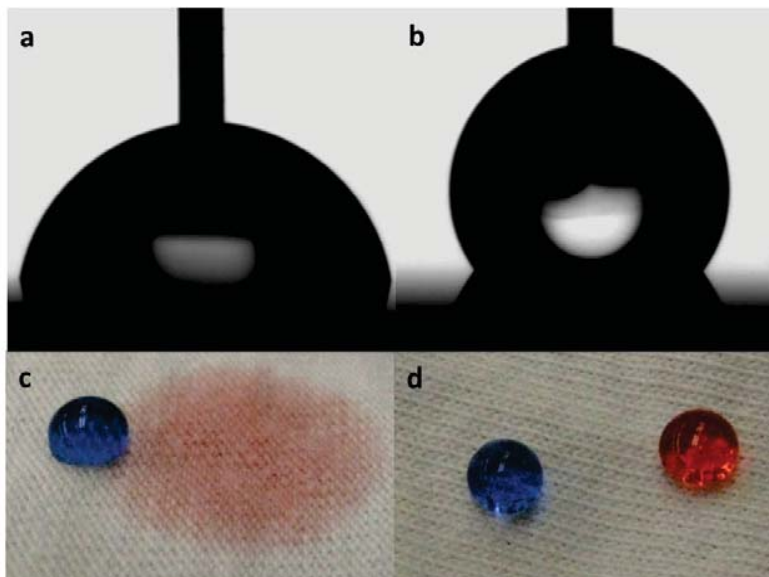
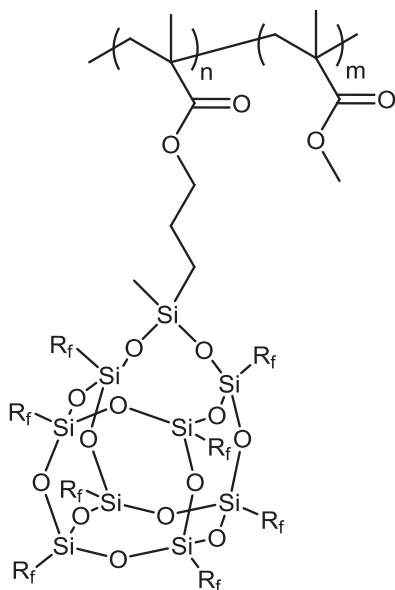
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# PMMA Copolymerization Summary



- Copolymerizations produced F-POSS based copolymers.
- Polymerization have trouble at higher F-POSS monomer feed ratios and are more controlled at lower conversion with RAFT initiator.
- Can we make homopolymer?



Static contact angle of a water droplet on a) 0 wt.% F-POSS copolymer or b) 25 wt.% F-POSS copolymer. Water (blue) and hexadecane (red) droplets on cotton fabric coated with c) 0 wt.% F-POSS copolymer and d) 25 wt. % F-POSS copolymer from 1% solution in Asahiklin-225.



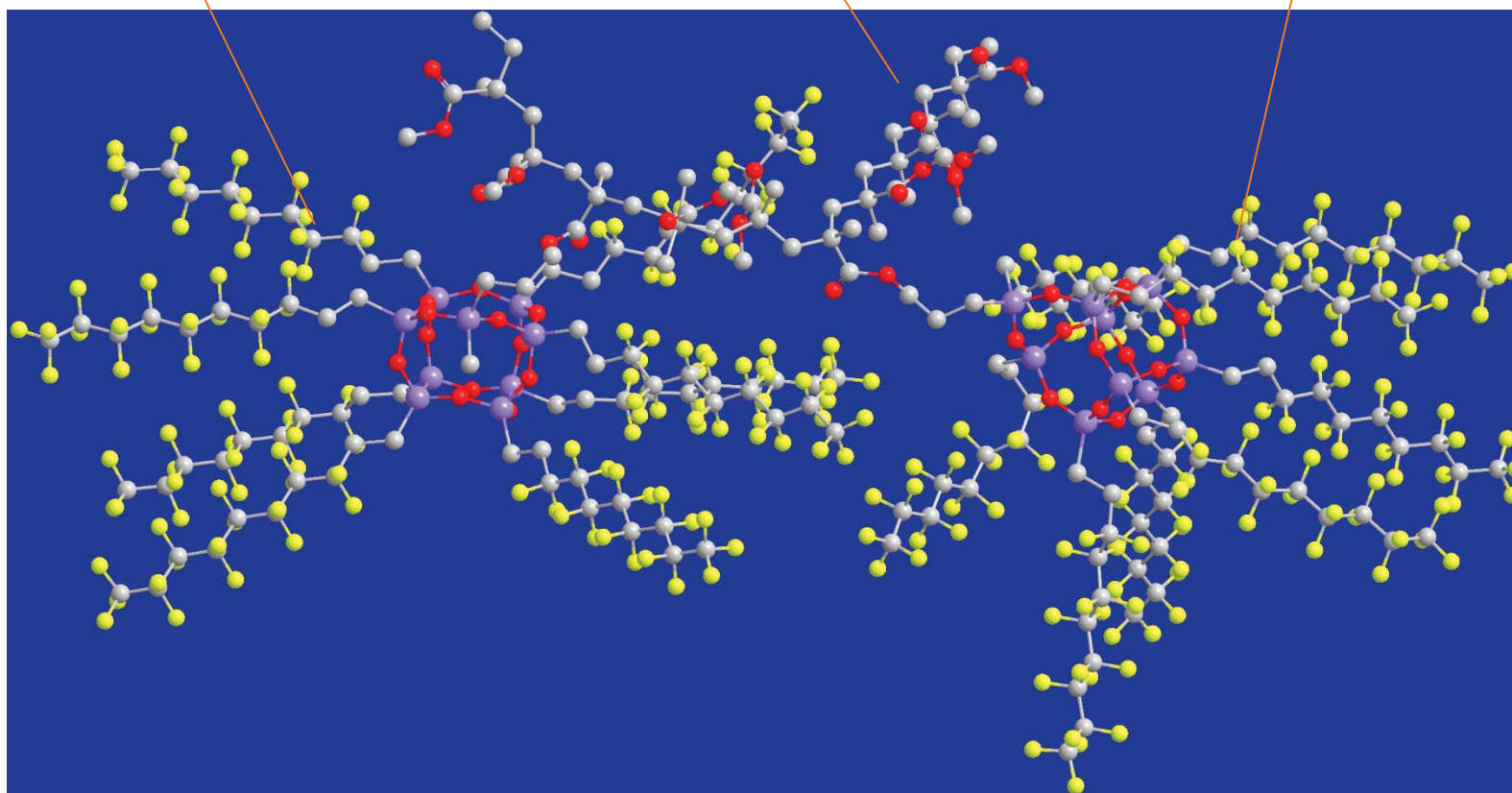


## Is it crowded in here?

F-POSS-MA

PMMA backbone (10 rpu)

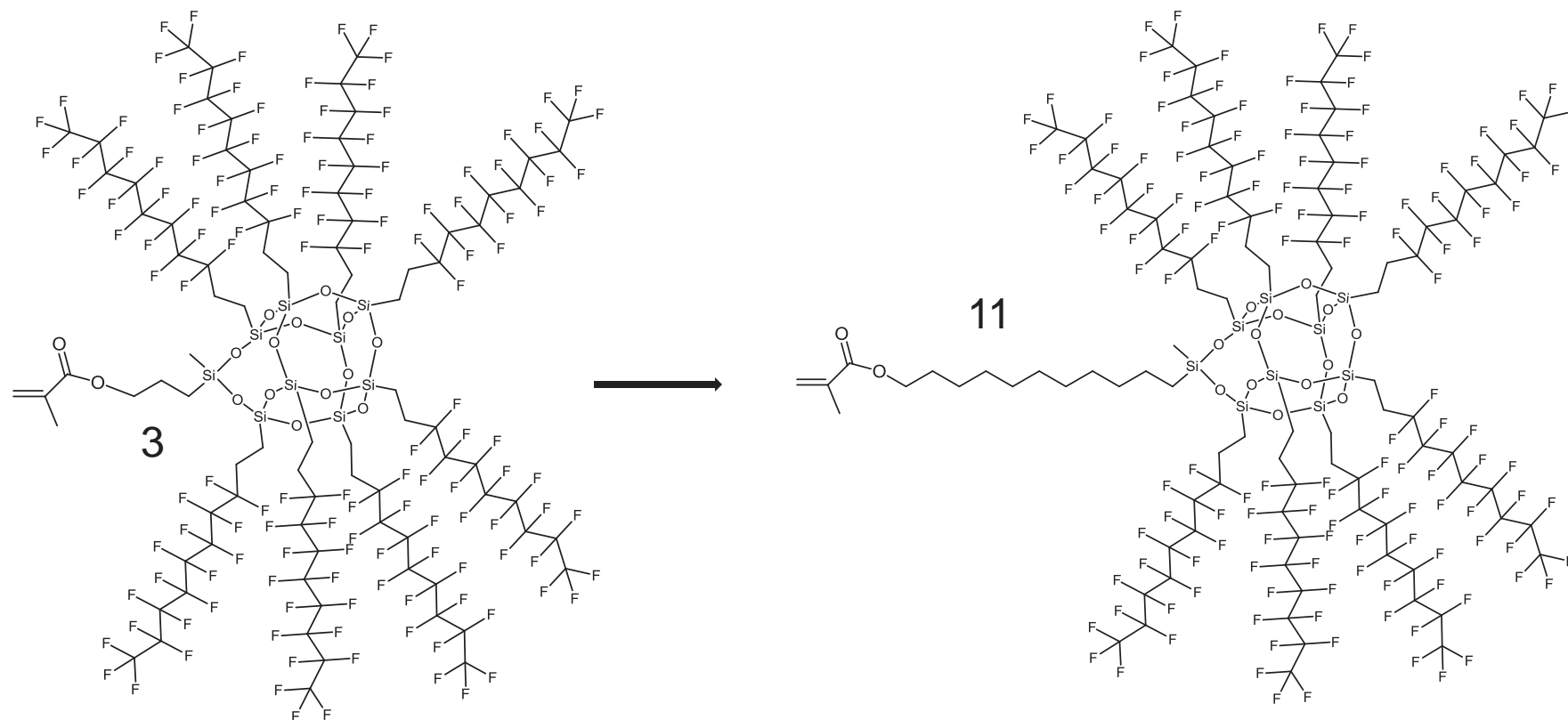
F-POSS-MA



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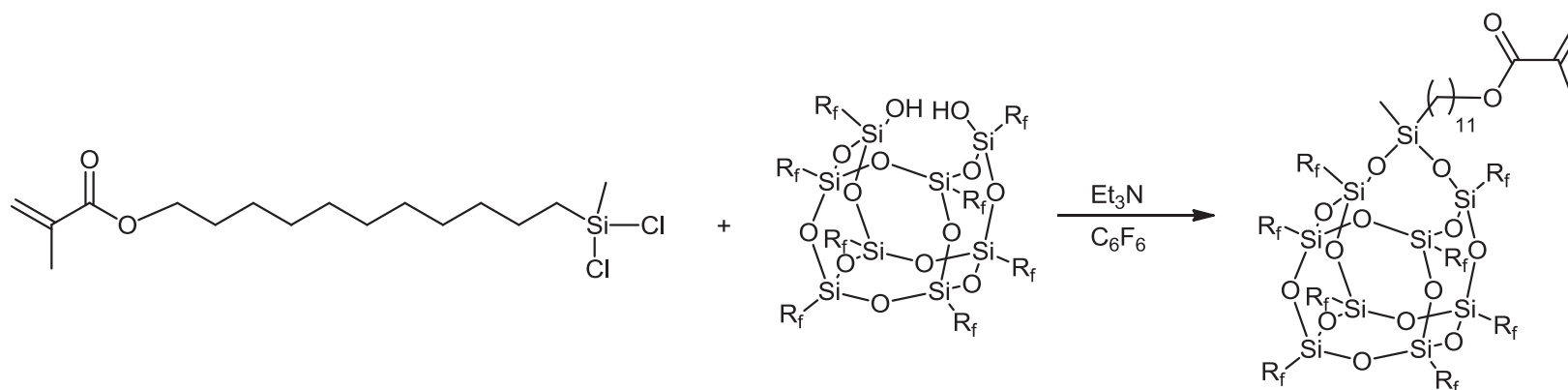
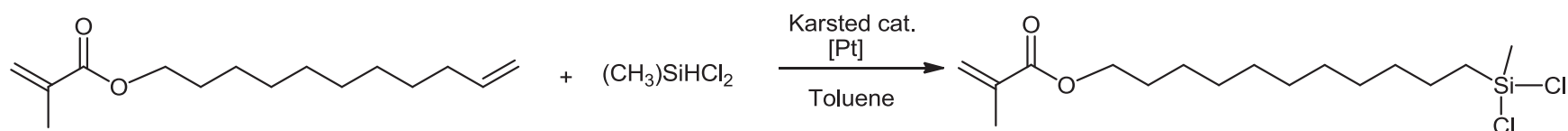
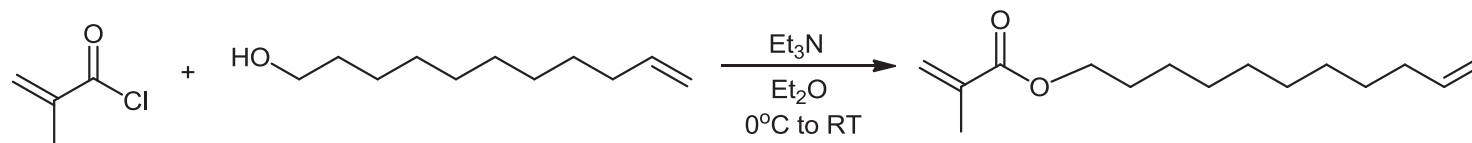


# Extend the Chain



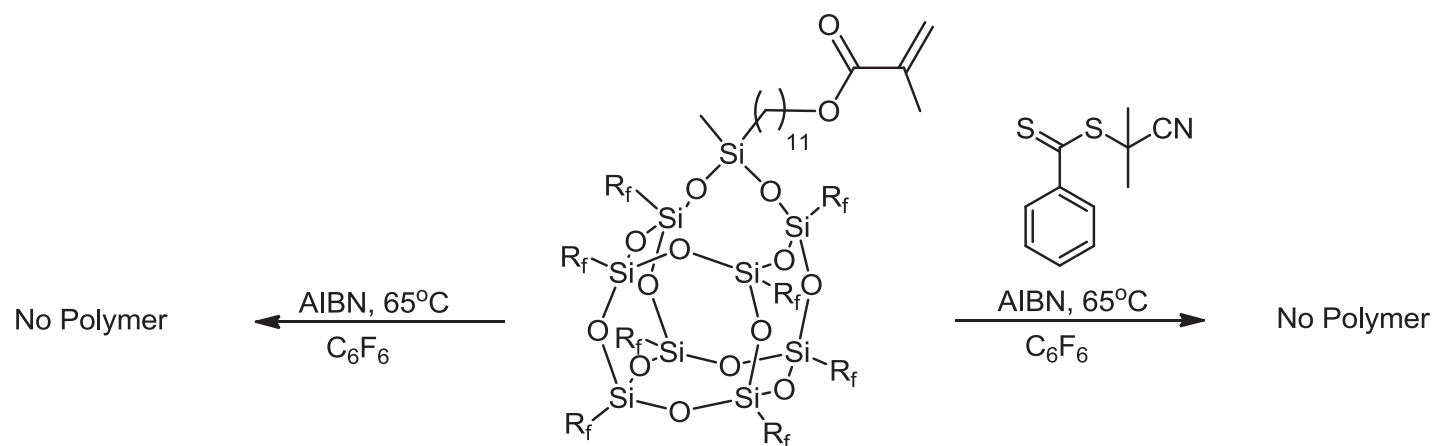


# Long Chain Monomer Synthesis





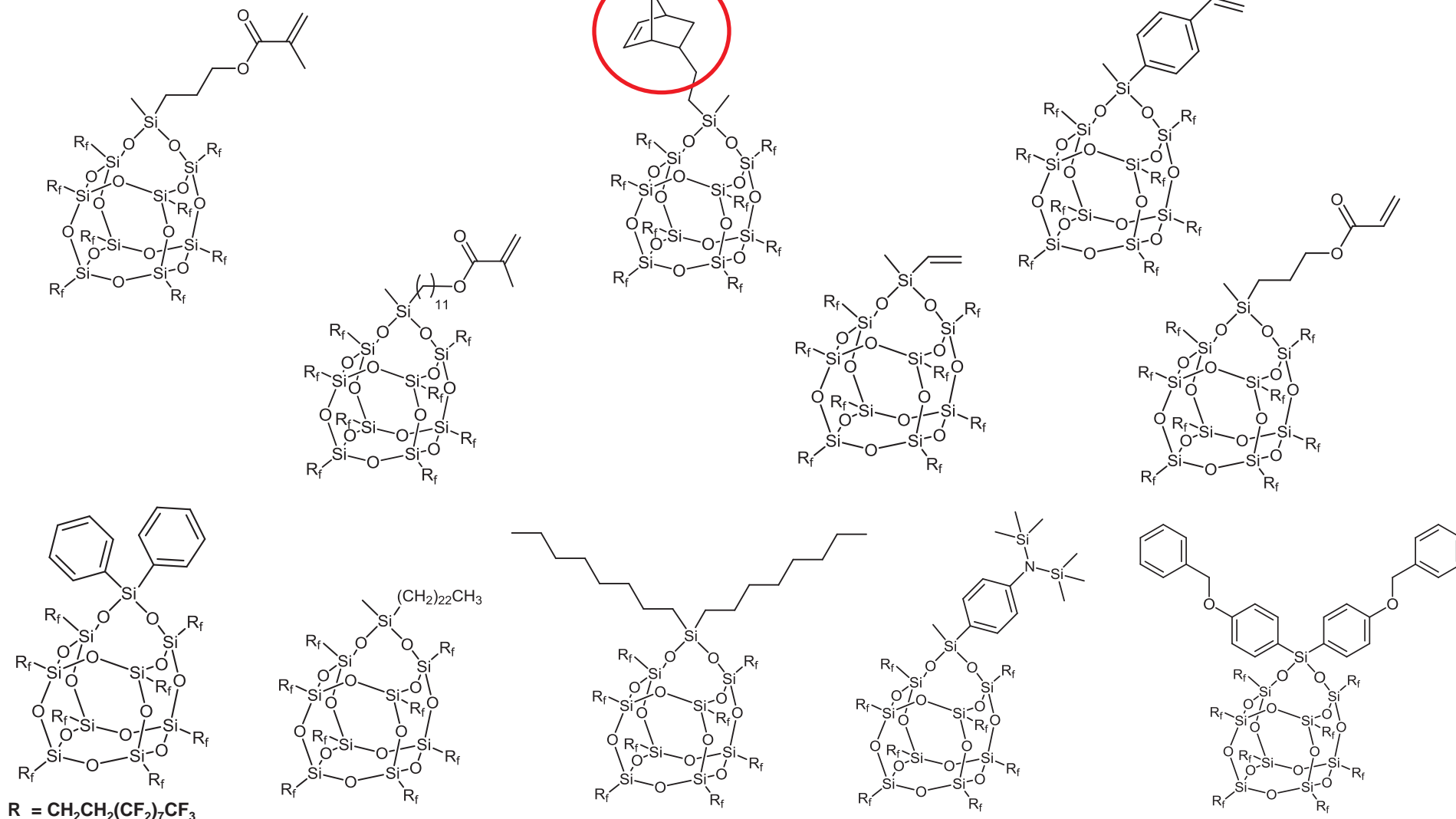
# Free Radical Polymerization



- No polymerization



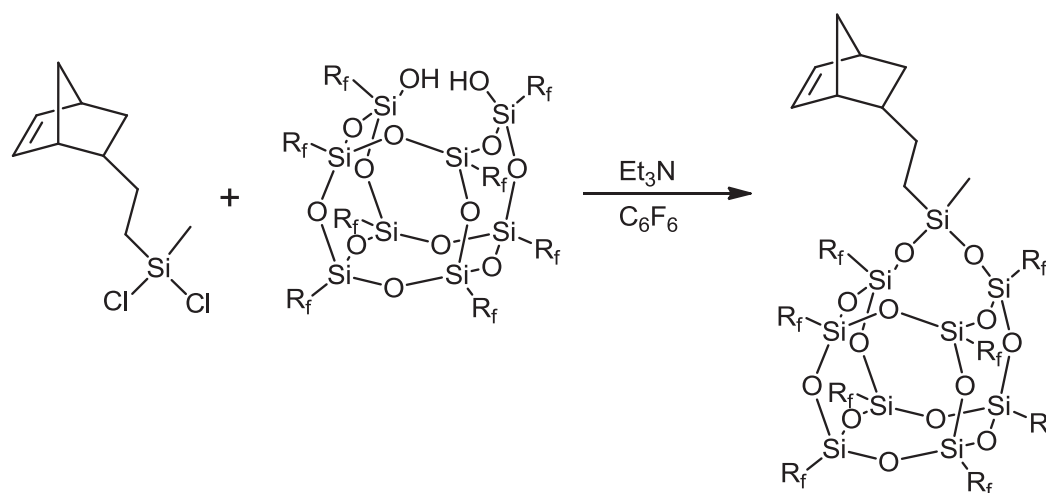
# F-POSS Structures Synthesized



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# Norbornene Synthesis

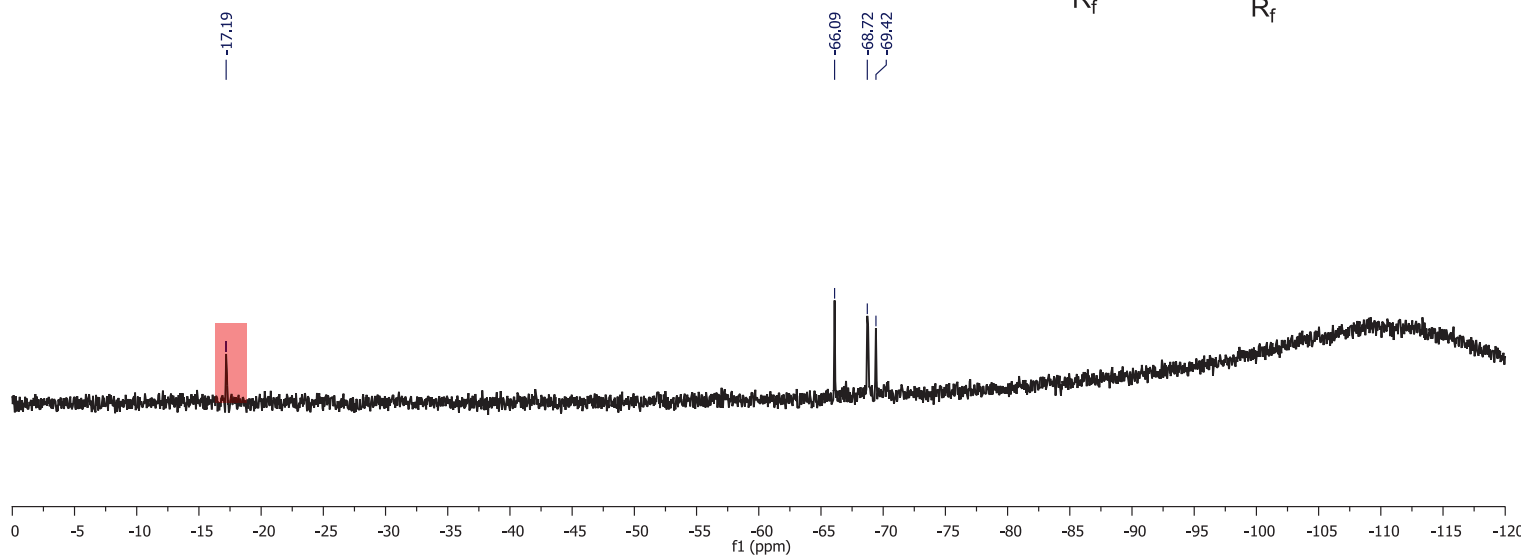
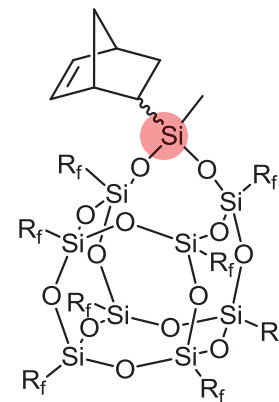
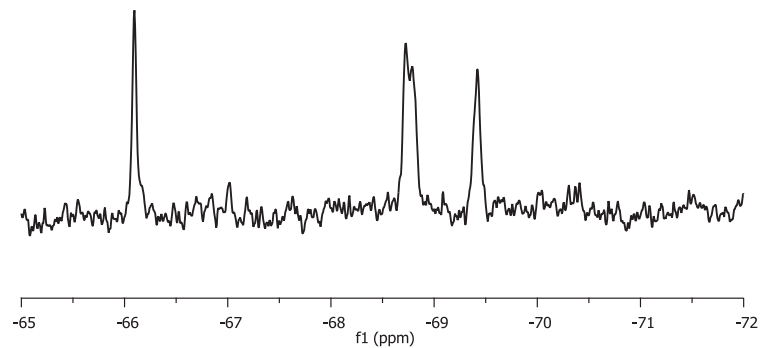


- Edge capping reactions typically have 52% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Norbornene functionalized F-POSS for ring opening metathesis polymerization (ROMP)





# $^{29}\text{Si}$ NMR

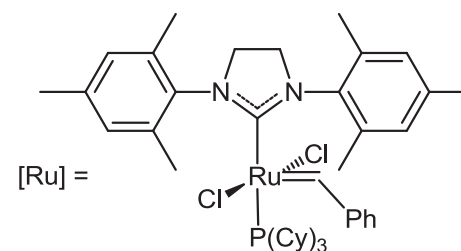
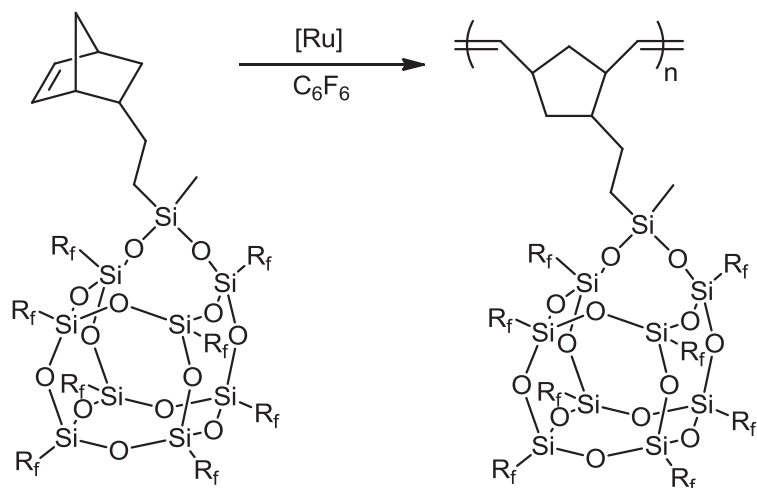


NMR:  $\text{CDCl}_3/\text{C}_6\text{F}_6$

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# ROMP (Norbornene)



Grubb's 2<sup>nd</sup> generation catalyst  
(soluble in hexafluorobenzene)

- Polymerization

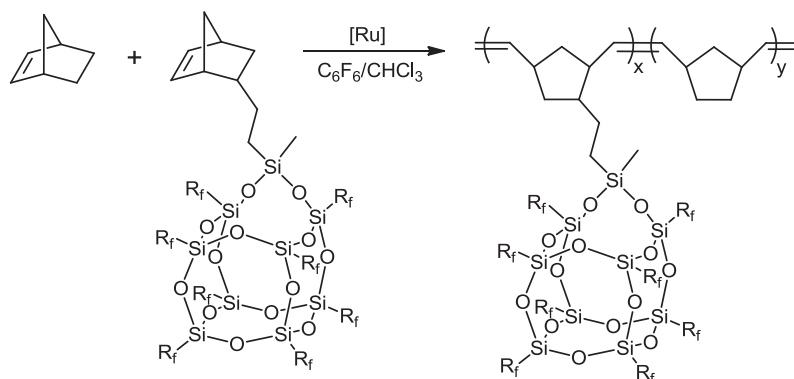
- Multiple polymerization in hexafluorobenzene
- 100:1, 50:1, 25:1 [monomer:catalyst]
- Reaction of 30 minutes (monitored by NMR)
- Higher monomer:catalyst ratios yield insoluble polymers
- Low  $T_g$  polymers ( $\sim 5^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  ramp rate) [polynorbornene  $\sim 35\text{-}60^\circ\text{C}$ ]
- Need a method to determine molecular weight

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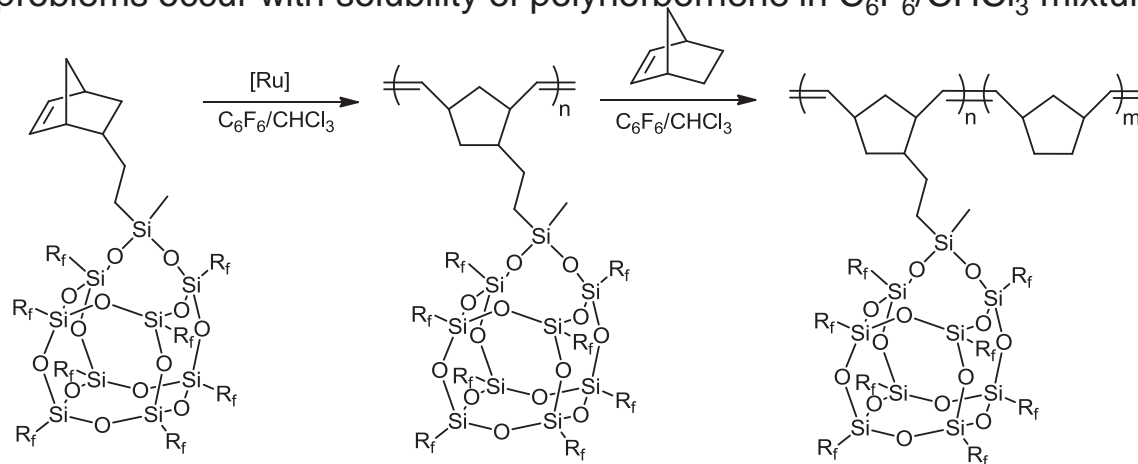


# ROMP (Copolymerization)

## Two Approaches



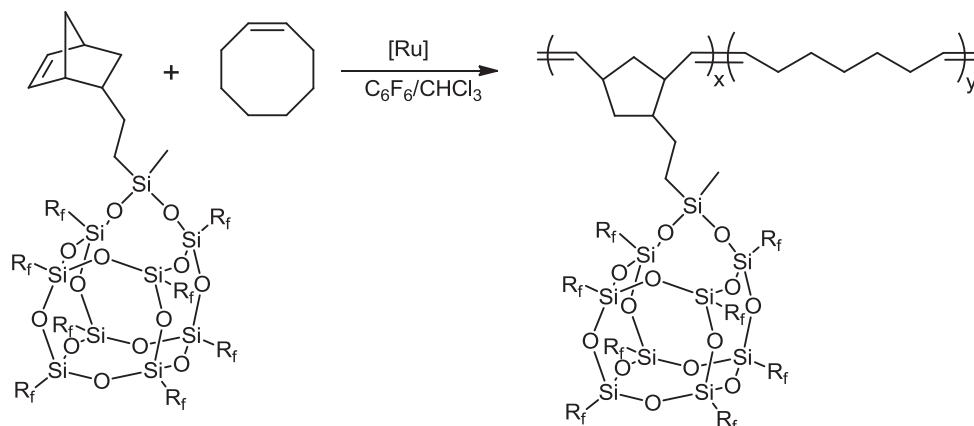
Random copolymer – problems occur with solubility of polynorbornene in  $C_6F_6/CHCl_3$  mixture.



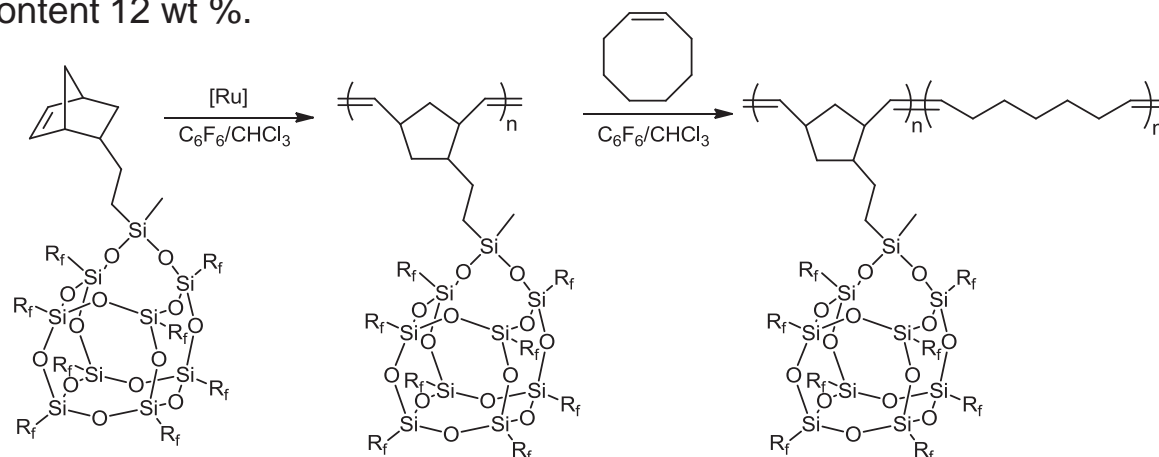
Block copolymers – keeping everything soluble remains a challenge here as well.



# ROMP (Cyclooctene)



Random copolymer – resulting polymers are soluble cyclooctene solvents (chloroform, THF, etc...) F-POSS content 12 wt %.



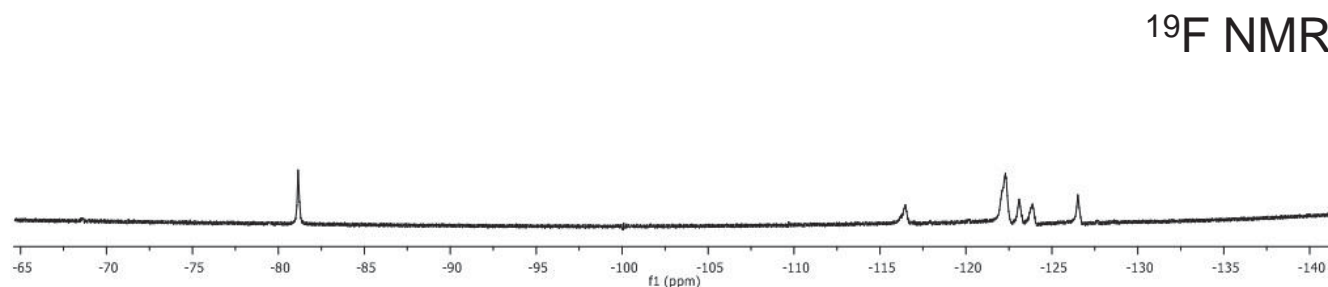
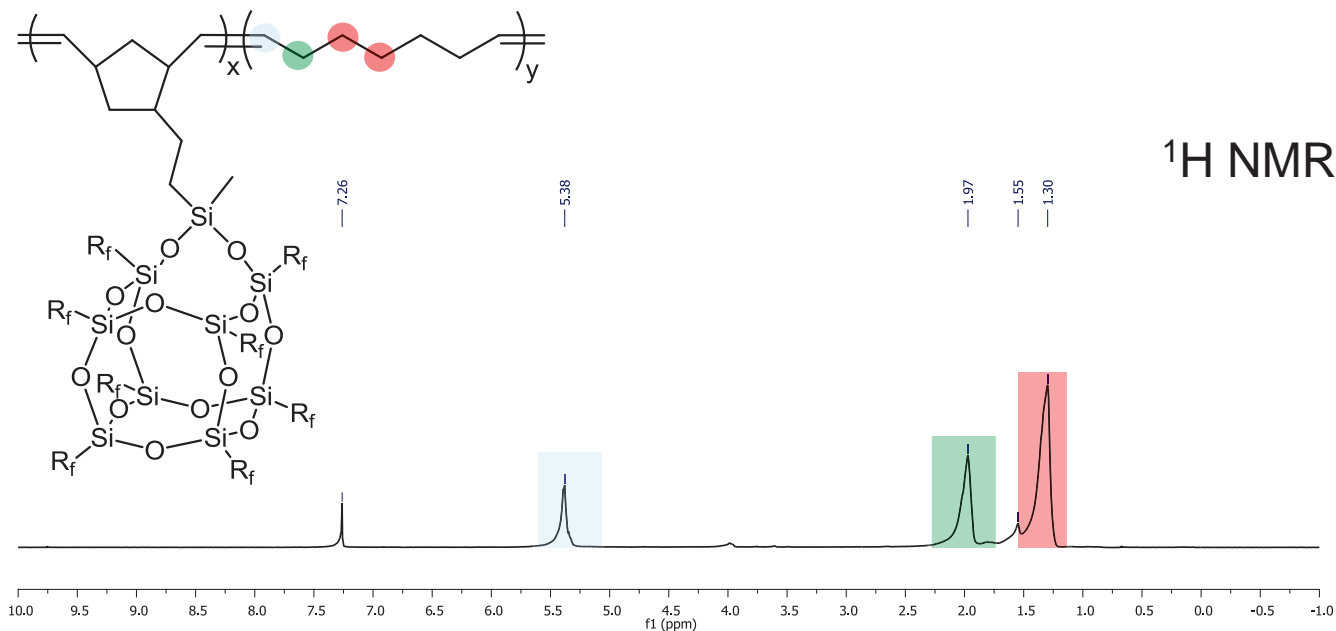
Block copolymers – resulting polymer is insoluble, possibly due to high molecular weight conversion F-POSS content 12 wt %.

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Liu, C.; Chun, S. B.; Zheng, L.; Haley, E.; Coughlin, E. B.; Mather, P. T., *Macromolecules* 2002, 35, 9868-9874. Alonso-Villanueva, J.; Cuevas, J. M.; Laza, J. M.; Vilas, J. L.; Leon, L. M., *Journal of Applied Polymer Science* 2010, 115, 2440-2447. Alonso-Villanueva, J.; Rodriguez, M.; Vilas, J. L.; Laza, J. M.; Leon, L. M., *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 2010, 47, 1130-1134.



# NMR of Copolymer



Polymer was precipitated in methanol, dissolved, and precipitated into asahiklin-225 before NMR.



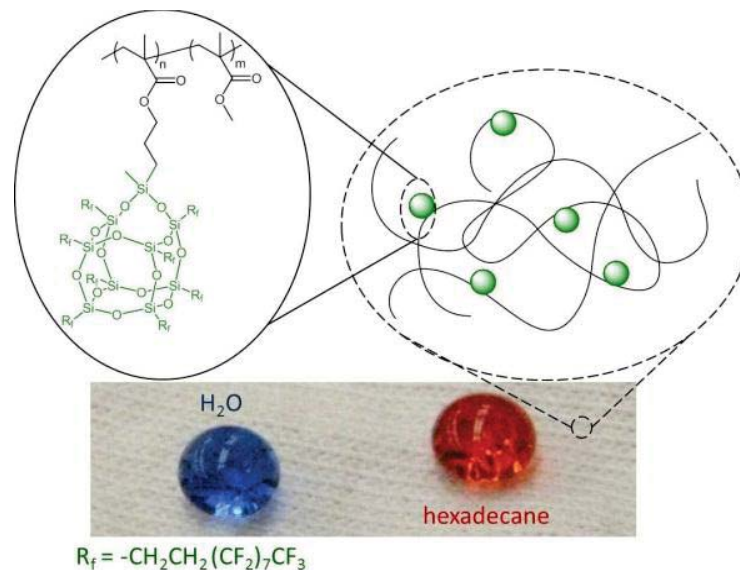
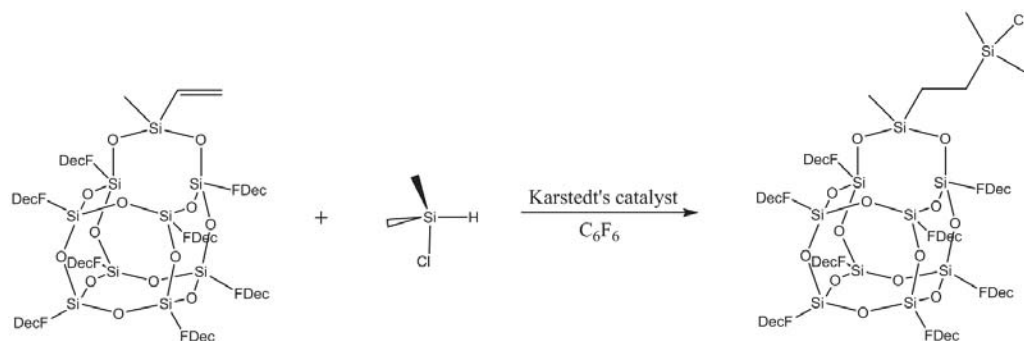
CDCl<sub>3</sub>

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# Summary

- RAFT copolymerizations were shown to be controlled and highly reproducible.
- ROMP polymerization works well. Work needs to be done with catalyst choice, solvent, and other reaction condition.
- F-POSS compounds have a near limitless potential in producing a variety of new hydrophobic, oleophobic, or ominiphobic polymer composites.
  - Reaction mechanisms, polymer composites, block copolymers, etc....







# Acknowledgements



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\*Former group member

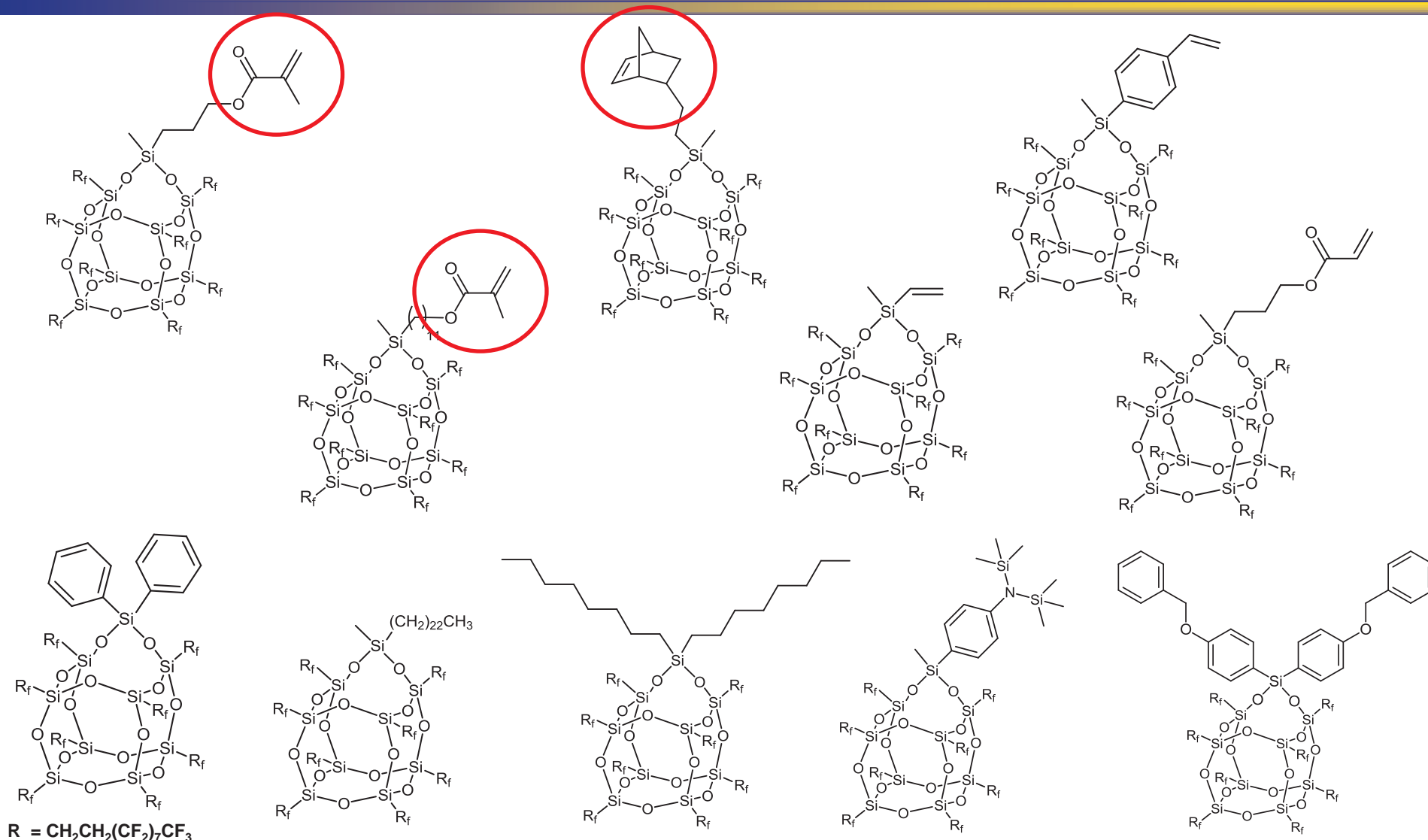
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# F-POSS Structures Synthesized



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